



Ion Exchange Behavior of Polyaniline and Polyaniline/ Silica Composite

Amirah Amalina Ahmad Tarmizi* and Muhammad Adam 'Azmi

Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor,
Malaysia

*Corresponding author email: amirahamalina@uitm.edu.my

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ABSTRACT

This study was conducted to compare the ion exchange behaviour of polyaniline (PANI) and polyaniline/silica (PANI/silica) composite. Rice husk silica (SiRH) was obtained from the combustion of rice husk ash followed by acid digestion method using sulfuric acid. Next, pristine PANI was synthesized via in situ oxidative polymerisation method using aniline and potassium dichromate in the acidic medium. Composite of PANI/SiRH was prepared with a similar method with the addition of SiRH in the process. Characterisations were done by employing X-Ray diffractometry and Fourier transform infrared spectroscopy. Polyaniline and PANI/SiRH composite were mixed with a solution containing Na^+ , Mg^{2+} , and K^+ . The concentrations of metal ions before and after contact with PANI and PANI/SiRH were measured using inductively coupled plasma-optical emission spectroscopy (ICP-OES). The effect of SiRH composition, contact time and pH on the ion exchange behaviour of PANI and PANI/SiRH composite was investigated. Results revealed that higher SiRH content in PANI/SiRH shows better ion-exchange properties with the optimum contact time of 30 minutes. The pH value of the metal ions decreased throughout the experiment.



Keywords: *rice husk, extracted silica, polyaniline composite, ion exchanger*

INTRODUCTION

Polyaniline (PANI) has become an attraction in the research world because of its wide applications in various field. However, there are some disadvantages of PANI that has been reported such as low solubility, low conductivity and low processability [1]. To overcome these problems, a filler is incorporated into the PANI matrix to enhance its thermal stability and mechanical characteristic compared to pristine PANI [2]. Many studies have been conducted to develop PANI composite for catalysis, adsorption, membrane separation, and analytical application [3]. PANI composite also can be applied as ion exchange for water treatment, especially for water softening [4]. The introduction of oxide filler, such as silica in the PANI structure will enhance the electrical, thermal and mechanical properties of PANI [5]. PANI silica composite compound will reveal better performance due to improved chemical stability [6].

Thus, various of inorganic and organic filler was incorporated with PANI to form PANI composite. PANI/ silica composites have the ability to remove metal ion from solution and mostly been widely practised as potential adsorbent for extraction of the metal contaminant in water. PANI alone is not enough as the polymer will aggregate when immersed in the solution. By adding filler, higher adsorption and ion exchange capacity can be observed. Most of the study used commercial filler to incorporate with PANI. In this study, silica extracted from rice husk (SiRH) was used as a filler to form PANI/SiRH composites. Using rice husk as a precursor for producing silica helps reduce disposal problem. This study aims to focus on the extraction of silica from rice husk, then incorporated to PANI and compared the ion-exchange ability of metal ion for PANI and PANI/SiRH composite.

METHODS

Materials and chemical

Rice husk, hydrochloric (HCl), potassium permanganate (KMnO₄), sulfuric acid (H₂SO₄), aniline, acetone, methanol, potassium dichromate (K₂Cr₂O₇), ammonium hydroxide (NH₄OH), sodium hydroxide (NaOH), potassium nitrate (KNO₃), sodium nitrate (NaNO₃), magnesium nitrate (Mg(NO₃)₂) and all chemicals were purchased from Sigma Aldrich.

Washing and Acid treatment

Rice husk was washed thoroughly with distilled water to remove dirt, dust and contaminant in the rice husk. Wet rice husk was dried in the oven at 110 °C for 24 h. Then, dried rice husk was refluxed with 50 mL of 0.1 M H₂SO₄ and stirred at 80°C. The treated rice husk was filtered and washed repeatedly with distilled water to remove residual acid from the mixture. Lastly, the rice husk was dried again for 24 hours at 110°C [7].

Extraction of silica

Rice husk was weighed (20 g) and burned in a furnace at 850 °C for two hours to obtain white rice husk ash [7], which was stirred in 50 mL of 1 M of NaOH solution for three hours. The solution was filtered and washed with 40 mL boiling distilled water. Then, the transparent and colourless solution was allowed to cool down to room temperature. Next, 2 M of H₂SO₄ and 1 M of NH₄OH were separately stirred at room temperature for three hours. 50 mL of 2 M of H₂SO₄ and 50 mL 1 M of NH₄OH were added into the colourless solution. Then the solution was filtered and washed with distilled water repeatedly to remove residual NH₄OH from the final mixture [7].

Synthesis of PANI and PANI/SiRH composites

PANI and PANI/SiRH composites were prepared by in situ oxidative chemical polymerisation. 0.1 M of HCl was added into 9.3 mL of aniline in a glass beaker. Then, the mixture was stirred for 10 min to allow homogenous doping by HCl. This step, was followed by the addition of potassium dichromate and the solution was stirred for two hours at 0 – 4 °C. After that, the solution was washed with distilled water, acetone and methanol to recover the PANI precipitate followed by drying at 60 °C [8]. Composite PANI/SiRH was prepared with the same method by adding silica from rice husk (SiRH) into the mixture after the addition of the HCl solution. Four different weight ratios of SiRH were added (0g, 0.2 g, 0.4 g, 0.6 g). The aniline-HCl will be deposited on the surface of SiRH due to the attraction force between the positive charge of the SiRH and aniline [8]. PANI and PANI/SiRH composite were characterised by using Fourier transform infrared spectroscopy (FTIR) and X-Ray Diffraction (XRD).

FTIR ANALYSIS

FTIR analysis was conducted by using a Perkin Elmer FTIR Model 2000 spectrophotometer at Faculty of Applied Sciences, UiTM Shah Alam. The FTIR spectra were performed on KBr pellets. The FTIR spectra were recorded from 500 to 4000 cm⁻¹ at 4 cm⁻¹ resolution.

XRD ANALYSIS

XRD data were collected to observe the effects of SiRH on the morphology of PANI. The analysis was performed using an XRD model PAN Analytical at Faculty of Applied Sciences, UiTM at ambient condition. The samples were scanned in the range of $10^\circ \leq 2\theta \leq 60^\circ$.

Ion exchange behaviour of PANI and PANI/ SiRH composite

Standard solutions containing 10 mg/L of mixed metal ion solution of Na⁺, Mg²⁺, and K⁺ was prepared by using analytical grade standards of

KNO₃, NaNO₃, Mg(NO₃)₂. 0.05 g of PANI was added into the conical flask containing 50 mL metal ion standard solutions at ambient temperature. The pH of the solution was recorded. The content was agitated using thermostat shaker thoroughly for 30 min and at 200 rpm. The PANI was filtered from the solution after 30 min. The concentration of the metal ion solution was measured using ICP-OES. The similar procedure was repeated with PANI/SiRH to study the metal-ion extraction. The investigation was carried out by varying the contact time (30 min, 60 min, 120 min, 180 min) and the amount of SiRH in the PANI (0 g, 0.2 g, 0.4g, 0.6g) [9].

pH

pH meter was used to analyse the pH of the solution after the experiment and during the experiment to observe the pH changes of the mixed metal-ions solution. pH value at different contact time (30 min, 60 min, 120 min, 180 min) was taken to observe the pH changes.

RESULTS AND DISCUSSIONS

Characterisation of PANI and PANI/SiRH composite

FTIR Analysis

FTIR analysis of SiRH, PANI and PANI/SiRH composites was conducted to identify the presence of the functional group in the samples. Figure 1 shows the FTIR spectra of SiRH, PANI and PANI/SiRH (0.6 g). The SiRH shows a characteristic peak at 3392 cm⁻¹ and 1040 cm⁻¹ which was attributed to stretching vibration of the Si–OH, Si–O–Si (asymmetric and symmetric) [10]. Next, PANI shows characteristic peaks at 3315 cm⁻¹, 2989 cm⁻¹, 1604 cm⁻¹, and 1456 cm⁻¹. The band at 3315 cm⁻¹ corresponds to the N–H stretching of aniline ring. The band at 2989 cm⁻¹ indicates aromatic C–H stretching while the band at 1604 cm⁻¹, and 1456 cm⁻¹ correspond to the quinoid and benzenoid ring of the PANI [10]. As for PANI/SiRH composite, most of the spectra of PANI/SiRH composites

correspond with the main characteristic peaks of PANI and SiRH peaks with slightly shift of wavenumber. The characteristic peak of Si-O-Si can be observed at 1029 cm^{-1} .

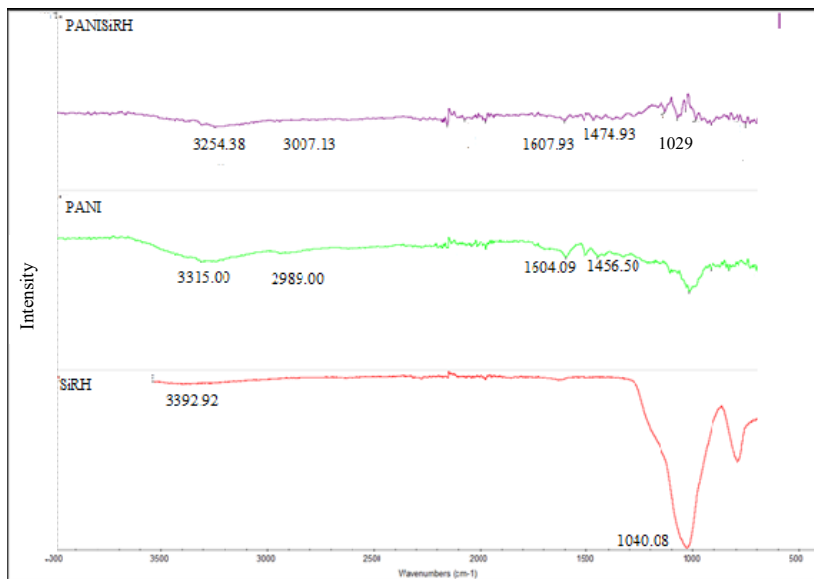


Figure 1: The FTIR Analysis of SiRH, PANI and PANI/SiRH (0.6g)

XRD analysis

Figure 2 shows the XRD analysis of SiRH, PANI and PANI/SiRH. A strong peak is observed at $2\theta = 23^\circ$. The presence of a broad strong peak in this region showed that SiRH is amorphous [11]. For PANI/SiRH composites, the broad peak of SiRH seems to overlap with the amorphous pattern of PANI. At $2\theta = 23^\circ$, there is a peak observed at PANI/SiRH composites, showing that the peak corresponds with the broad peak of SiRH. However, the intensity of the peak decreased, and this confirms the adherence of PANI with SiRH [12]. Besides, no peak was observed for PANI, which revealed that the polymer is amorphous [13].

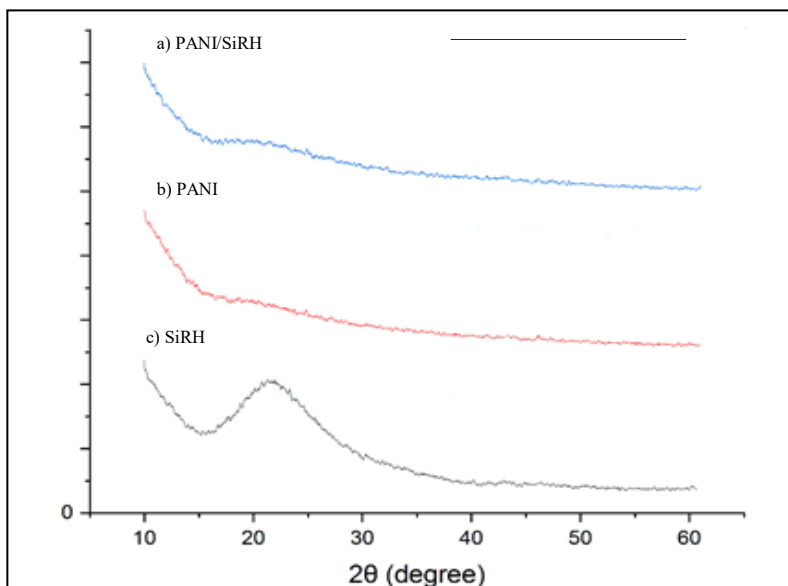


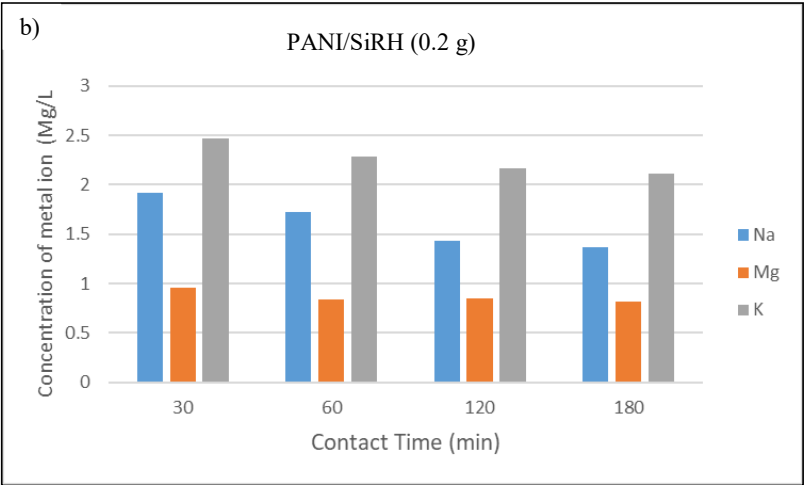
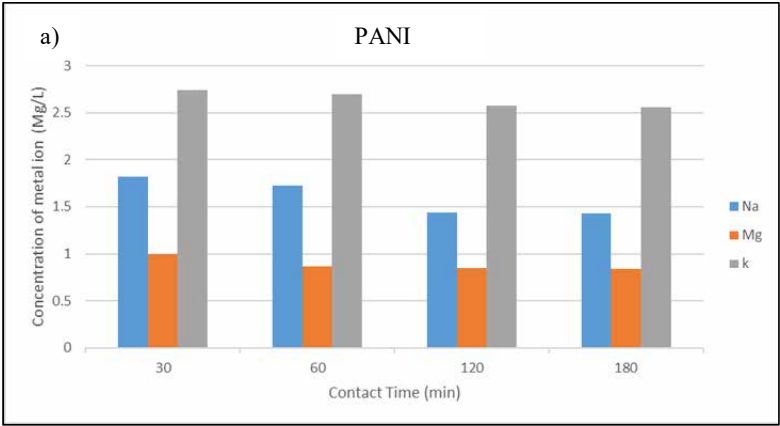
Figure 2: XRD Spectra for a) PANI/SiRH, b) PANI c) SiRH

ION EXCHANGE BEHAVIOUR OF PANI AND PANI/SiRH

Effect of contact time

Figure 3 shows the concentration of metal ions as a function of contact time for PANI and PANI/SiRH composites. The analysis revealed that all PANI and PANI/SiRH composites exhibited the highest adsorption at 120 min, and insignificant depletion was found at the subsequent contact hours. Thus, the optimum adsorption time of Na and K metal ions by all PANI/SiRH composite sample is at 120 min. and for Mg metal ions the optimum adsorption by PANI/SiRH composite is at 60 min. The higher uptake of metal ions is probably due to the high surface availability of PANI/SiRH for adsorption [14]. On the other hand, slight depletion at subsequent hours probably due to the surface of the PANI/SiRH polymer, which had

become saturated and metal ions are forced to diffuse only to the internal pore structure of PANI [3].



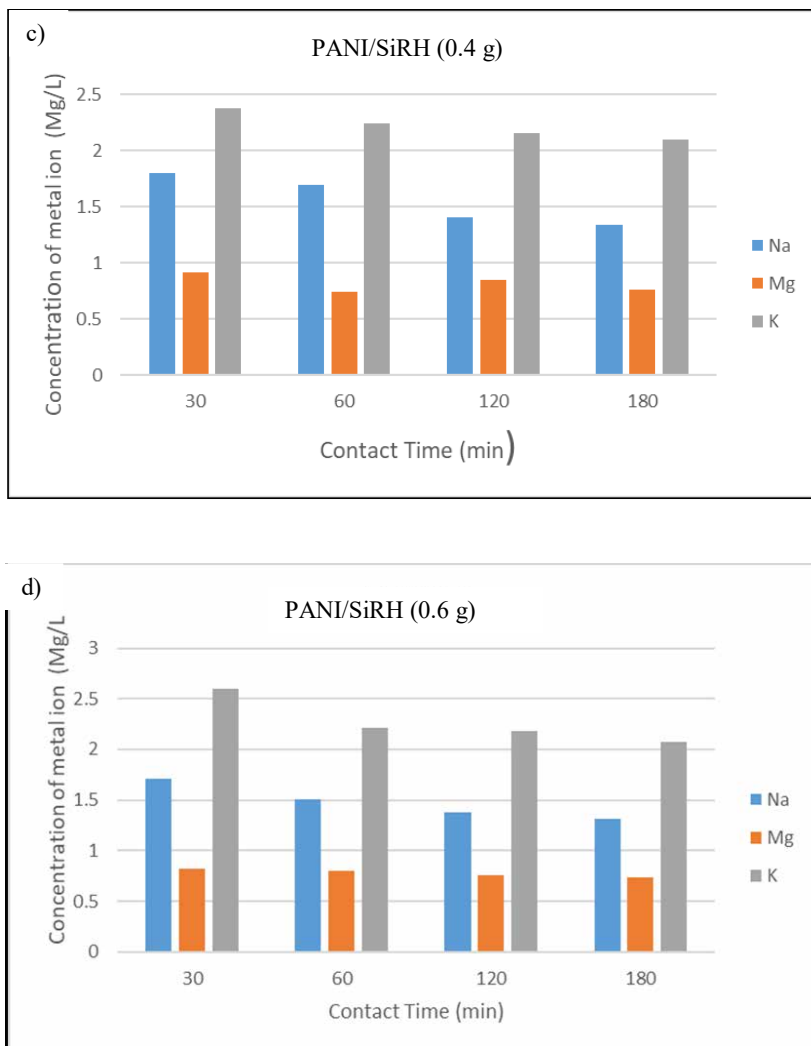


Figure 3: The Concentration of Metal Ion Adsorbed by a) PANI b) PANI/SiRH (0.2 g) c) PANI/SiRH (0.4 g) and d) PANI/SiRH (0.6 g) for Various Contact Time

EFFECT OF TYPES OF METAL -IONS ON PANI AND PANI/SIRH ADSORPTION

Figures 3d shows the effect of metal -ions type on PANI and PANI/SiRH (0.6 g) adsorption. PANI/SiRH (0.6 g) was chosen as it shows the highest metal-ions absorption at 30 min. It can be seen from the figure, that type of metal ion affects the absorption ability of PANI. The highest removal of the metal is magnesium (92%), followed by sodium (86%) and lastly potassium (78%). This trend can be explained as every metal ion has a different size of particles. So, the particle size can affect the amount of particle adsorbed on the surface of the polymer matrix. The magnesium ion has a smaller particle size (0.62 Å) compared to sodium ion (0.98 Å). Potassium ion has the largest radii (1.33 Å) among the three metal ions used in this study. This finding is aligned with Al-Senani et al. [15], they have suggested that as the cation radii decreased, the metal ions adsorption increased. This phenomenon was due to the adsorption of metal ions at the internal surface area of PANI. Smaller particles size had high rates of adsorption at the internal surface. This is because, at the internal surface, the transfer of metal ions through the pores occurred rapidly [15]. Thus, for bigger metal particle ion it is difficult to diffuse through the pore, and metal ions only adsorb at the external surface of the PANI [16].

EFFECT OF SILICA (SiRH) CONTENT

In this experiment, PANI/SiRH composites with different amount of fillers ranged from 0 to 0.6 g (PANI/SiRH (0.6)) was added into the mixed metal ions solution of sodium (Na), magnesium (Mg), and potassium (K). Results show that the amount of SiRH incorporated with PANI affects the amount of metal ions adsorption. As shown in Figure 4, the concentrations of metal ions decrease as the amount of extracted SiRH added into the PANI increased. Lower concentration of mixed metal ions revealed better absorption of metals by the samples. PANI shows the highest metal ions concentration because it adsorbed fewer metal ions compared to PANI/SiRH (0.6). PANI/SiRH (0.6) adsorbed more metal ions compared to other samples because fewer metal ions left in the metal ions solution. The amount of SiRH added into PANI has caused changes on the surface chemical composition

of PANI. SiRH affect the interaction between the metal ions particle with a polymer matrix (PANI) become stronger [17]. SiRH increased the surface area of PANI, thus, increasing the number of metal-ions particles to adsorb or exchange on the PANI surface.

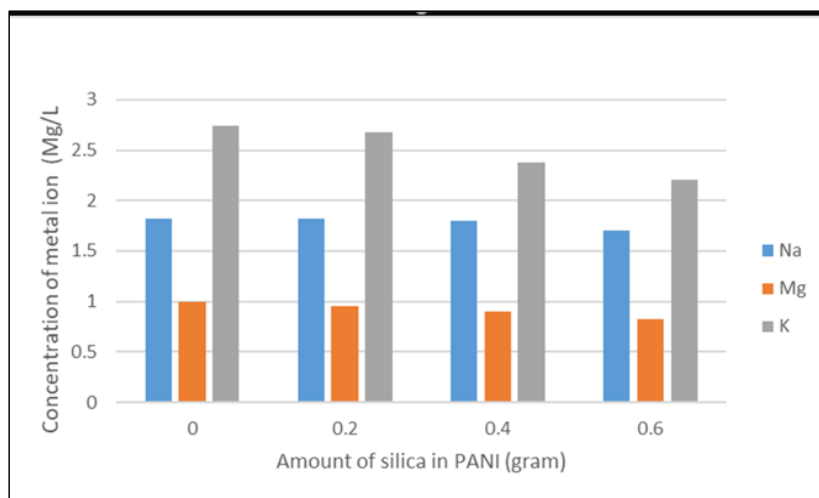


Figure 4: The Concentration of Mixed Metal Ions for PANI and PANI/Composite

PH STUDY

Table 1: pH Value of the PANI and PANI Composite at Different Contact Time Time (min)

Sample	SiRH content	Time (min)				
		0	30	60	120	180
PANI	0	7.15	6.80	6.80	6.8	6.8
	0.2	7.15	6.80	6.78	6.77	6.7
	0.4	7.15	6.80	6.79	6.78	6.78
	0.6	7.15	6.70	6.70	6.70	6.70

pH study was conducted to observe the pH changes of metal ions solution during the adsorption of metal ions on the polymer matrix. pH was taken before and during the experiment to see whether the metal ions solution

becomes more acidic or basic. Table 1 shows the pH value of PANI and PANI/SiRH composite at 0, 30, 60, 120 and 180 min. The pH of the solution before the experiment is 7.15. However, during the experiment, the pH value decreases and reached equilibrium at 6.7. Both PANI and PANI/SiRH revealed the same trend. However, for PANI/SiRH (0.6 g), the pH value reaches equilibrium after 30 min. The decrease of pH was caused by the ion exchange mechanism between the H^+ ion from the polymer with the metal ion which is positively charged [18]. In the metal ion solution, H^+ was released from the polymer and metal ions will replace the H^+ at the polymer structure [18]. From the pH results, for PANI/SiRH (0.6 g) the ion exchange behaviour is faster compared to others. After 30 minutes, the value already constant. This result support that SiRH increased the surface area of PANI, hence, more of the metal ions particles will adsorb or exchange on the PANI surface [19].

CONCLUSION

In conclusion, PANI and PANI/SiRH were successfully synthesized by using the chemical oxidative method. FTIR confirms the successful incorporation of SiRH into PANI matrix. In addition, XRD revealed the amorphous nature of PANI and PANI/SiRH samples. PANI/SiRH composite with 0.6 g SiRH revealed the highest adsorption of metal ion compared to other composites. Therefore, it can be concluded higher SiRH content in PANI will increase the ion exchange ability of the conducting polymer.

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